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Enhanced Oil Recovery: Chemical Flooding

Ahmed Ragab and Eman M. Mansour

Abstract

The enhanced oil recovery phase of oil reservoirs production usually comes after the water/gas injection (secondary recovery) phase. The main objective of EOR application is to mobilize the remaining oil through enhancing the oil displacement and volumetric sweep efficiency. The oil displacement efficiency enhances by reducing the oil viscosity and/or by reducing the interfacial tension, while the volumetric sweep efficiency improves by developing a favorable mobility ratio between the displacing fluid and the remaining oil. It is important to identify remaining oil and the production mechanisms that are necessary to improve oil recovery prior to implementing an EOR phase. Chemical enhanced oil recovery is one of the major EOR methods that reduces the residual oil saturation by lowering water-oil interfacial tension (surfactant/alkaline) and increases the volumetric sweep efficiency by reducing the water-oil mobility ratio (polymer). In this chapter, the basic mechanisms of different chemical methods have been discussed including the interactions of different chemicals with the reservoir rocks and fluids. In addition, an up-to-date status of chemical flooding at the laboratory scale, pilot projects and field applications have been reported.

Keywords: enhanced oil recovery, EOR, chemical flooding, alkaline, surfactant, polymer, interfacial tension, IFT

1. Introduction

The Average oil recovery after the primary recovery phase is about 5–20% of the original oil in place (OOIP) and can be increased by applying the secondary recovery phase up to 40%. Usually, the EOR application stage will be after the secondary recovery when the main challenge is not the reservoir pressure only, but also the reservoir fluids relative mobility compared to the injected fluids during the secondary recovery phase [1].

There are different EOR methods such as thermal recovery, miscible Gas Injection, Chemical flooding and Microbial EOR as shown in **Figure 1**. This chapter covers the fundamentals and the mechanisms of the recovery enhancement of the chemical flooding EOR as one of the main EOR methods [2]. The feasibility study and design for EOR projects require integrated work between different disciplines such as reservoir engineers, petroleum geologists, petrophysicists, geomodellers, chemical engineers, and production engineers whom are responsible to start with the screening phase of the different EOR methods and come up with the shortlisted one in order to go for the next step which is lab testing phase that requires PVT/core labs capable to implement the various EOR lab tests,

then, analyze the lab scale results to be coupled with the reservoir simulation model in order to estimate the incremental recovery for the different EOR methods under study. For any EOR project, the initial stage is the screening criteria in order to identify the best EOR application for the candidate reservoirs in terms of incremental recovery that will be added and the economics of the project [3]. For any EOR project, the initial stage is the screening criteria in order to identify the best EOR application for the candidate reservoirs in terms of incremental recovery that will be added and the economics of the project. The screening criteria is based on both reservoir rock and fluids properties such as oil gravity, oil viscosity, oil composition, remaining oil saturation (target), formation type, reservoir thickness, depth, and temperature. In **Table 1**, a summary of screening criteria for the chemical EOR methods based on lab and applied field data. So, in this chapter we are assuming that the screening criteria was done and it has been found that the chemical flooding is the optimum EOR method that can be applied for the reservoir under study [4].

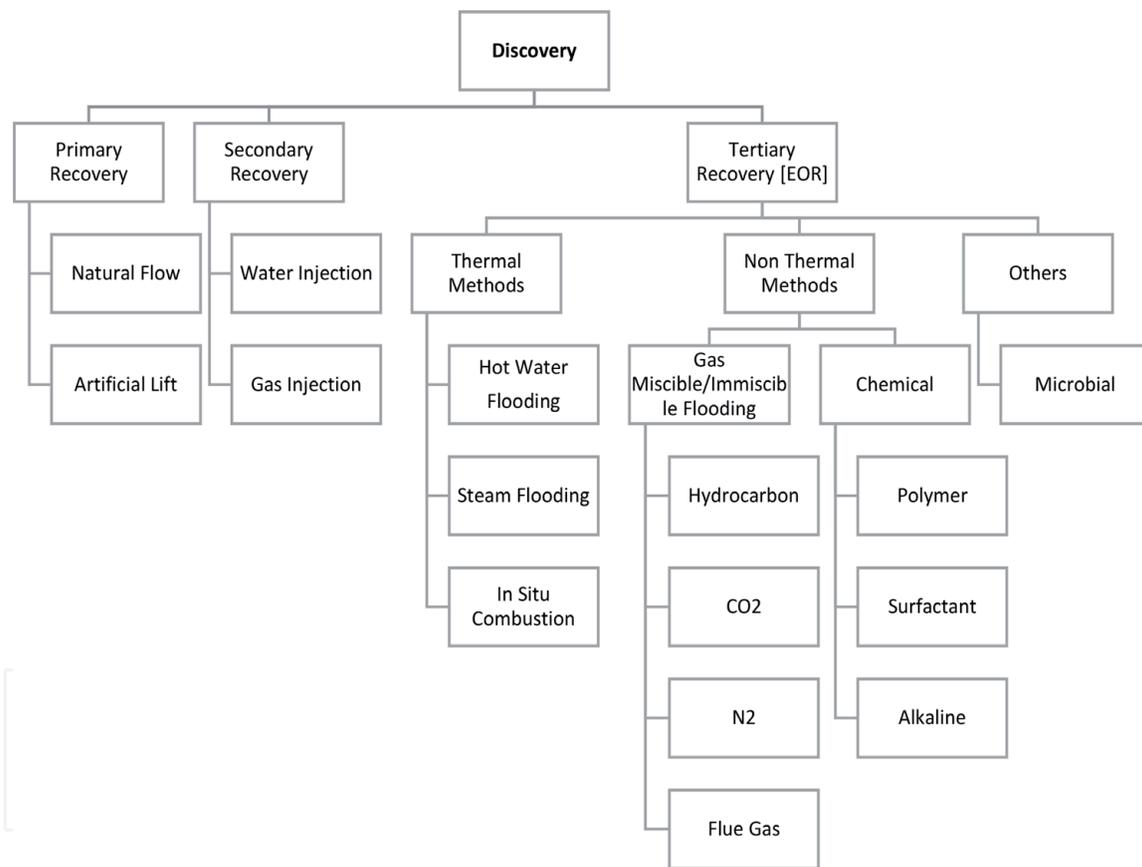


Figure 1.
Oil production mechanisms.

EOR Method	Oil Gravity ($^{\circ}$ API)	Viscosity (cP)	Oil Saturation (%)	Formation Type	Reservoir Thickness (ft)	Average Permeability (mD)	Depth (ft)	Temperature ($^{\circ}$ F)
Polymer Flooding	> 15	<150 & >10	>50	Sandstone is preferred	NC	>10	<9000	>200
Micellar/Polymer, ASP, and Alkaline flooding	> 20	<35	>35	Sandstone is preferred	NC	>10	>9000	>200

Table 1.
A summary of screening criteria for the chemical EOR methods.

2. Chemical EOR flooding classification

The chemical flooding EOR can be categorized into the following:

1. Polymer flooding.
2. Surfactant flooding.
3. Surfactant-polymer flooding.
4. Alkaline flooding.
5. Alkaline-surfactant-polymer flooding.

The next sections of this chapter will discuss individually each method in order to illustrate the fundamentals, the reservoir-fluids interactions processes, and the field applications [5].

2.1 Polymer flooding

In concept, a water-soluble polymer is used to reduce the mobility ratio of water-oil by increasing the water viscosity which improves the volumetric sweep efficiency. The mechanism of polymer flooding is to increase the water viscosity and also to reduce the permeability of the rock to water, in other words, to reduce the water-oil mobility ratio close to unity or less [6]. Over the past years, polymer floods projects have been applied over a wide range of conditions:

- Reservoir temperatures [46–235]°F.
- Average reservoir permeability [0.6–15,000] mD.
- Oil viscosity [0.01–1494] cP.
- Net pay thickness [4–432] ft.
- Remaining oil at start-up [36–97] % of OOIP.

Polymers have been used in oil production in three modes; as near-well treatments to improve the performance of water injectors or watered out producers by blocking off high conductivity zones, agents that may be cross-linked in situ to plug high conductivity zones at depth in the reservoir and agents to lower water mobility or water-oil mobility ratio. Polymer flooding is suited for reservoirs where normal water floods fail due to one of the two reasons: High Heterogeneity and High oil water mobility ratio which is targeting the oil in areas of the reservoir that have not been contacted efficiently [7]. The main economic limitation is the cost of polymers is. For example, if the cost of acrylamide/acrylate copolymers and xanthan polymers were substantially lower and higher polymer concentrations with larger polymer flood bank sizes could be granted in a given application. It would improve oil-recovery efficiencies, wider ranges of potential applications, and higher profits. Polymer flooding is showing promising results, specifically, if flooding projects are started at high remaining oil saturations. Polymer flooding has been conducted in sandstone and carbonate reservoirs, and oil-wet, water-wet, and mixed-wettability reservoirs [8].

2.1.1 Mechanism

The main effect of the polymer is the enhancement of the water-oil mobility ratio to be unity or less, the mobility ratio is defined as the ratio of the mobility of displacing phase to the mobility of displaced phase which is calculated from the following equation [6].

$$M_{w-o} = \frac{M_w}{M_o} = \frac{K_w}{K_o} * \frac{\mu_o}{\mu_w} = \frac{K_{rw}}{K_{ro}} * \frac{\mu_o}{\mu_w} \quad (1)$$

where

M_{w-o} : the water - oil mobility ratio

M_w : the water mobility

M_o : the oil mobility

K_w : the effective permeability to water, mD

K_o : the effective permeability to oil, mD

μ_o : the oil viscosity, cP

μ_w : the water viscosity, cP

K_{rw} : the relative permeability to water

K_{ro} : the relative permeability to water

As per this equation, it is clear that in order to drive the mobility ration to be unity or less, the water viscosity is increased by adding the water-soluble polymers to the injected water as shown in **Figure 2**, when the displacing fluid (water) viscosity is lower than the oil, the recovery efficiency decreases as the remaining oil after this flooding is about 45% of the OOIP at 0.1 viscosity ratio. On the other hand, once the viscosity ration reached to 1 (polymer added to water) the remaining oil after the flooding will be reduced to 20% of the OOIP. As summary, the highest viscosity ratio is the highest oil recovery [9].

2.1.2 Polymer flooding advantages

The advantages of polymer flooding could be summarized as following [10]:

- I. Applicable over a wide range of conditions.
- II. A reduction in the quantity of water required to reduce the oil saturation to its residual value in the swept portion of the reservoir.
- III. An increase in the areal and vertical coverage in the reservoir due to a reduced water flood mobility ratio.
- IV. Diverting the injected from swept zones.
- V. Promising for heavy oil application.
- VI. Cost-effective.

Polymer flooding limitations are:

- I. High oil viscosities require a higher polymer concentration.
- II. Results are normally better if the polymer flood is started before the water-oil ratio becomes excessively high.

III. Clays increase polymer adsorption.

IV. Some heterogeneity are acceptable, but avoid extensive fractures.

V. Lower injectivity than with water can adversely affect oil production rates in the early stages of the polymer flood.

VI. Xanthan gum polymers cost more, are subject to microbial degradation, and have a greater potential for wellbore plugging.

2.1.3 Field projects statistical data of some polymer flooding

A summary statistical data for field projects of polymer flooding as shown in Table 2.

2.2 Surfactant flooding

Correctly designed surfactants can create micro emulsions at the interface between oil and water phases, which cause a reduction in the interfacial tension (IFT) that consequently will mobilize the residual oil which improving the oil recovery as shown in Figure 3. This method of EOR is a challenging one by many factors such as rock adsorption of the surfactant and co-surfactant, and the chromatographic separation of the surfactant during the injection in the reservoir. The designed surfactants should be resistant and active at reservoir conditions which could be at higher pressure, temperature and water salinities [11]. In the surfactant flooding the phase behavior is the most important factor to make it successful. Currently, there is no EOS model to describe the phase behavior in these systems. Consequently, phase behavior studies should be observed experimentally which is challenging to mimic the reservoir conditions. Surfactants solutions are used to reduce the oil-water IFT, while the co-surfactants are mixed with these solutions in order to enhance the properties of the surfactant solutions. The co-surfactants added to the solutions are serving as an active agent or a promoter

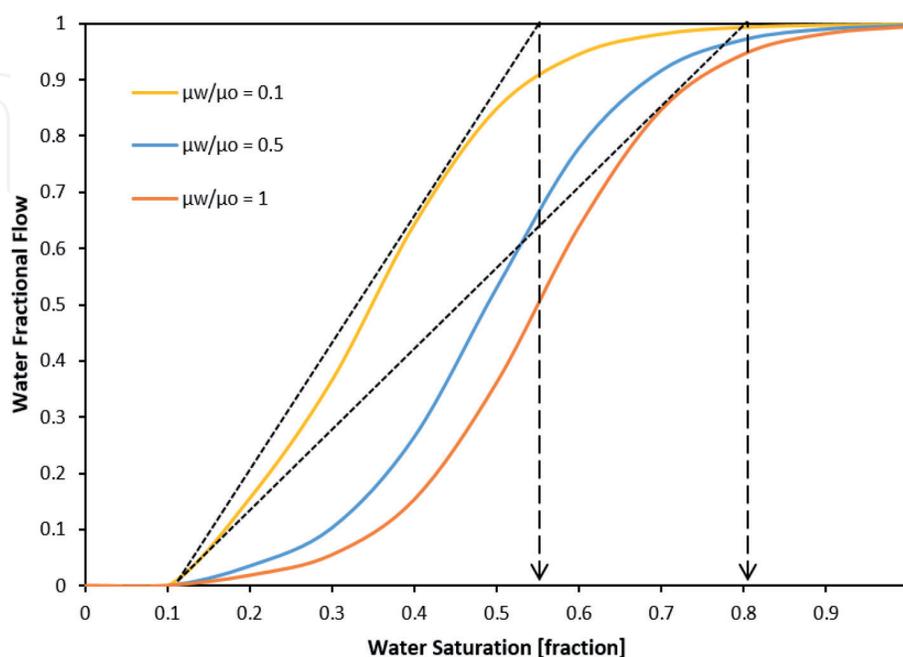


Figure 2.
Effect of viscosity ratio on the fractional flow curve.

Parameter(s)	No. of Projects	Mean
Depth, ft	87	4000
Temperature, F	88	117
Permeability, mD	80	453
Oil Viscosity, cP	82	21.5
Polymer Concentration, ppm	48	279
Oil Recovery, % OOIP	20	4

Table 2.
A summary of statistical data for field projects.

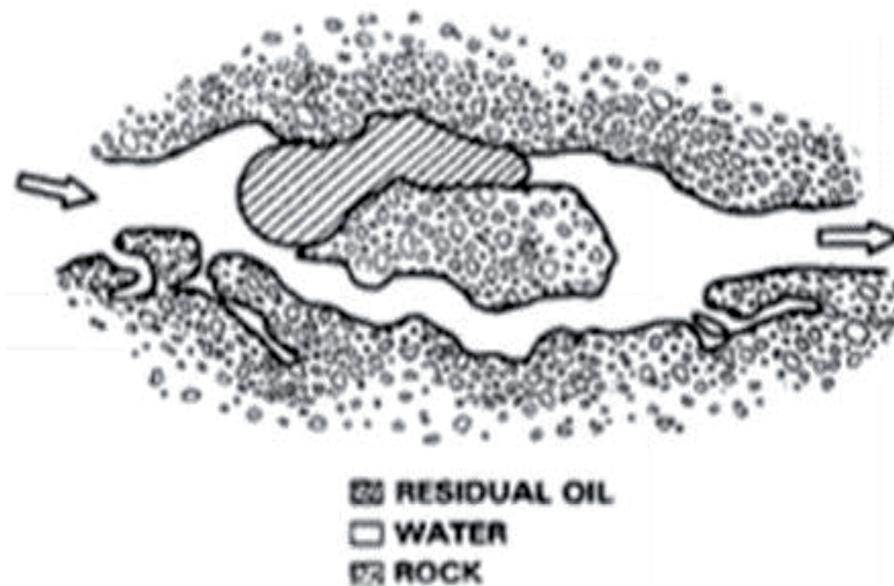


Figure 3.
Principle of flooding, where residual oil is trapped in the reservoir; for the movement of oil through the narrow capillary pores, very low oil/water interfacial tension (IFT) is required.

in the mixed solution in order to enhance the surfactant effectiveness with respect to temperature and water salinity as it is well known that surfactant flooding is sensitive to reservoir temperature and salinity [6].

2.2.1 Mechanism

A surfactant is added to an aqueous fluid and co-surfactant is also added in order to prepare the surfactant solution and injected into the reservoirs as surfactant flooding reduces the interfacial tension between the oil and water phases and also alters the wettability of the reservoir rock in order to mobilize the residual oil trapped in the reservoir which improves the oil recovery as shown in **Figure 3** [12].

The surfactant selection is a critical stage in designing the surfactant flooding projects as the Anionic surfactants preferred due to the following reasons [13]:

- Low adsorption at neutral to high pH on both sandstones and carbonates.
- Can be tailored to a wide range of conditions.

- Widely available at low cost in special cases.
- Sulfates for low temperature applications.
- Sulfonates for high temperature applications.
- Cationic can be used as co-surfactants.

On the other hand, the Non-ionic surfactants have not performed as well for EOR as anionic surfactants. Sulfonated hydrocarbons such as alcohol propoxylate sulfate or alcohol propoxylate sulfonate are commonly used for Surfactant flooding.

2.2.2 Surfactant flooding advantages

The surfactant flooding has several advantages and some of them are listed below [5]:

1. Very effective in lab test [high oil recovery].
2. Surfactant modeling is relatively simple with only a few well-designed experiments needed to provide the most important simulation parameters.
3. Current high-performance surfactants cost less than \$2/lb. of pure surfactant.
4. Recent developments in surfactants solutions for EOR have effectively reduced the required surfactant concentration which lowering the chemical costs required.
5. Recently, new and effective surfactants are derived from plant resources such as sunflower oil, soy and corn oil. It is non-toxic, non-hazardous, and readily biodegradable.

The disadvantages of surfactant flooding could be listed as following:

1. Complex and expensive system.
2. Possibility of chromatographic separation of chemicals.
3. High adsorption of surfactant.
4. Losing its effectiveness at higher pressure, temperature, and salinity.

2.2.3 Field projects of the surfactant flooding

Many technically successful pilots have been done in addition to several small commercial projects have been completed and several more are in progress. Relatively, homogeneous reservoir formation is preferred. The presence of high amounts of clays, gypsum, or anhydrite is undesirable. For commercially available surfactants, formation-water chlorides should be less than 20,000 ppm and divalent ions (Ca^{++} and Mg^{++}) should be less than 500 ppm. The problems encountered with some of the old pilots are well understood and have been solved and the new generation surfactants will tolerate high salinity and high hardness so there is no practical limit for high salinity reservoirs [14].

2.3 Surfactant-polymer (SP) flooding

Surfactant-polymer flooding process is injecting a chemical slug that contains water, surfactant, electrolyte (salt), usually a co-surfactant (alcohol), followed by polymer-thickened water. In this process a surfactant is added to the polymer solution that has the affinity for both water and oil. The use of the micellar solution is to reduce the interfacial tension of the water-oil system in the reservoir in order to displace the residual oil [15]. SP flooding method was patented for Marathon oil co. by Gogarty and Tosch known as Mara-flood. The injection profile of the method consists of injecting a pre-flush (to achieve the desired salinity environment), followed by micellar slug (surfactant, co-surfactant, electrolyte), and followed by polymer solution along with drive water.

The micellar solution composition that ensures a gradual transition from the displacement water to the displaced oil without interface is as following [13]:

- Surfactant 10–15%.
- Water 20–60%.
- Oil 25–70%.
- Co-surfactant 3–4%.

Usually, the co-surfactant is alcohol which enhances the possibility for the micellar solution to include oil or water. This surfactant-polymer flooding reduces the oil-water IFT through the surfactant portion and reduces the mobility ratio through presence of polymer.

2.3.1 Mechanism

The micellar solution is prepared using inorganic salts (water-soluble electrolytes) in order to gain better viscosity control of the solution. A polymer slug is used to drive the micellar solution slug in order to get a mobility control. The injection process is shown in **Figure 4**. The technique establishes low oil-water IFT and controls the mobility ratio which forming a considerable oil bank to be produced [11].

2.3.2 Surfactant-polymer flooding advantages

The SP flooding advantages are listed below:

- Interfacial tension reduction (improves displacement sweep efficiency).
- Mobility control (improves volumetric sweep efficiency).
- Reduce adsorption of expensive surfactants.

The disadvantages could be as follows:

- Complex and expensive system.
- Possibility of chromatographic separation of chemicals.

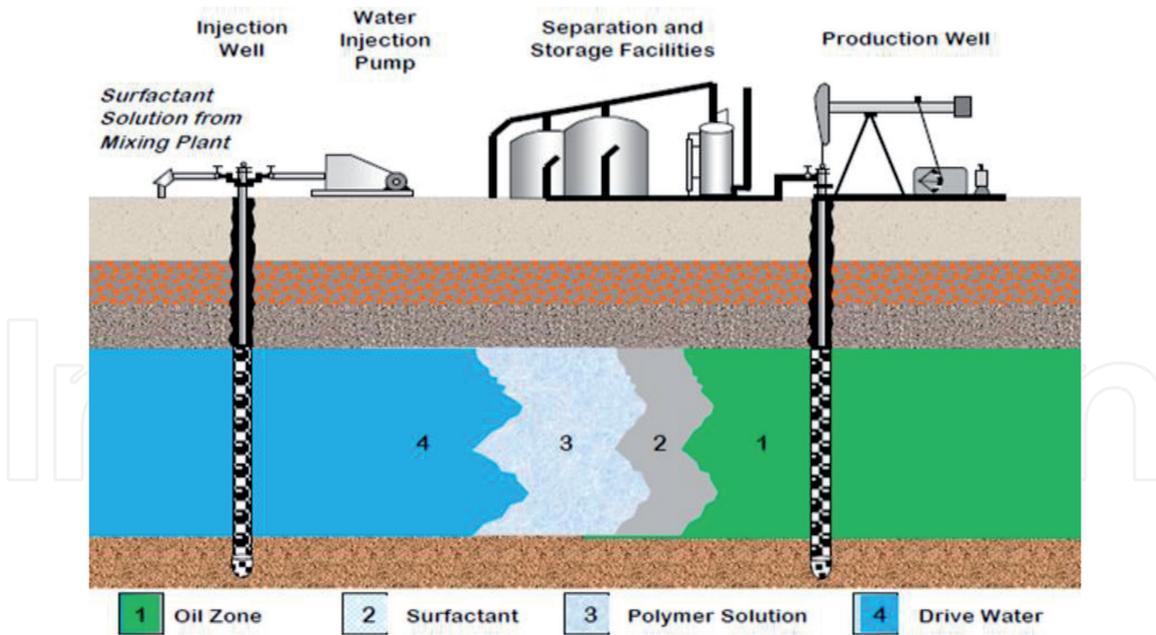


Figure 4.
Surfactant-polymer injection process.

- High adsorption of surfactant.
- Interactions between surfactant and polymer.
- Degradation of chemicals at high temperature.

2.3.3 Field project of the surfactant-polymer flooding

Since 1990, polymer flood and SP flood have been applied in a few field pilots and expanded field tests.

2.4 Alkaline flooding

Alkaline flooding is one of the EOR methods in which alkaline agents are injected into the reservoir to produce in situ surfactants, so the alkaline flooding will eventually have the same effect of the surfactant flooding.

2.4.1 Mechanism

In the Alkaline flooding process, the alkaline agents such as sodium hydroxide solution is injecting into the reservoirs which react with the naturally occurring organic acids in the oil in order to produce surfactants or soaps at the oil-water interface. However, the alkaline agents are less expensive than the surfactant agents, the expected incremental oil recovery by alkaline flooding has not been confirmed by field results and still remains possibility as the process is mainly dependent on the mineral composition of the reservoir rock and its oil [11].

2.4.2 Alkaline flooding advantages

This EOR method has the same advantages of the surfactant flooding in addition to that its main advantage over the surfactant is the cost of the alkaline agents are cheap compared to the surfactant agents [12].

2.4.3 Field project of the surfactant-polymer flooding

There were several pilot tests worldwide such as in Russian Tpezocephoe Field, Hungarian H Field, Whittier Field in California, and North Gujarat Oil Field, India.

2.5 Alkaline-surfactant-polymer (ASP) flooding

Individual chemical flooding processes, alkaline flooding, surfactant flooding and polymer flooding, can be combined differently. The three-component combination, alkaline surfactant-polymer (ASP). The ASP method represents a cost-effective chemical EOR method that yielding high oil recovery (mostly for sandstone reservoirs). ASP flooding is utilizing the benefits of three flooding methods, where oil recovery was enhanced, by reducing IFT, improving mobility ratio, and improving microscopic displacement efficiency. The ASP projects in China shows that the incremental oil recovery over water-flooding is 18.9% on the average [14].

2.5.1 Mechanism

Alkaline injection reduces surfactant adsorption and the combination of soap and synthetic surfactant results in low interfacial tension (IFT) in a wider range of salinity. Soap and surfactant make emulsions stable through reduced IFT which improve the sweep efficiency. There is a competition of adsorption sites between polymer and surfactant. Therefore, addition of polymer reduces surfactant adsorption, or vice versa and improves the sweep efficiency of ASP solution [5].

2.5.2 Alkaline surfactant-polymer flooding advantages

Several advantages can be summarized as follows:

- Alkali is inexpensive, so it is cost reduction factor.
- Alkali reacts with acid in oil to form soap.
- Provide lower IFT in a wide salinity range.
- Soaps and surfactants produce emulsions that improve the sweep efficiency.
- Polymer and alkaline are reducing the surfactant adsorption.
- The polymer addition improves the sweep efficiency of the ASP solution.
- Carbonate formations are usually positively charged at neutral pH, which favors adsorption of anionic surfactants. However, when (Na_2CO_3) is present, carbonate surfaces (calcite, dolomite) become negatively charged and adsorption decreases several fold.
- High pH also improves micro-emulsion phase behavior.

The limitations and challenges for ASP flooding are:

- Severe scaling in the injection lines with strong emulsification of the produced fluid.

- Polymers are less effective under high water salinity conditions, as the high salt waters degrade the viscosity of polymers.
- Mobility control is critical.
- Laboratory tests must be done with crude and reservoir rock under reservoir conditions and are essential for each reservoir condition.

2.5.3 Field projects of the alkaline surfactant-polymer flooding

There are large field trials that already implemented worldwide showing encouraging results. The following table (**Table 3**) shows a summary for the ASP projects or underway since 1980 including the start-up date, oil gravity, Oil viscosity, implementation phase as secondary or tertiary, oil recovered in % of OOIP, and the chemical cost in USD/bbl. In **Figure 3**, the production results after applying the ASP flooding at the end of the water-flooding phase [13].

Surfactant Enhanced Water Floods											
Alkaline Surfactant Polymer Projects Completed or Underway Since About 1980											
Field	Owner	Technical	Region	Start	API	Oil Viscosity - cp	Type	Pore Volume Chemical	Oil Recovered % OOIP	Chemical Cost/USD	Chemicals
Adena	Babcock & Brown	Surtek	Colorado	2001	43	0.42	Tertiary	In progress		\$2.45	Na2CO3
Cambridge	Barnett	Surtek	Wyoming	1993	20	25	Secondary	60.4%	28.07%	\$2.42	Na2CO3
Cressford	Dome	Surtek	Alberta	1987			Secondary			\$2.25	Alkali and Polymer Only
Daqing BS	Sinopec		China	1996	36	3	Tertiary	82.1%	23.00%	\$7.88	NaOH - Biosurfactant
Daqing NW	Sinopec	Surtek	China	1995	36	3	Tertiary	65.0%	20.00%	\$7.80	NaOH
Daqing PO	Sinopec	Surtek	China	1994	26	11.5	Tertiary	42.0%	22.00%	\$5.51	Na2CO3
Daqing XV	Sinopec		China		36	3	Tertiary	48.0%	17.00%	\$9.26	NaOH
Daqing XF	Sinopec		China	1995	36	3	Tertiary	55.0%	25.00%	\$7.14	NaOH
Daqing Foam	Sinopec		China	1997	NA	NA	Tertiary	54.8%	22.32%	\$8.01	ASP Foam Flood following WAG
Daqing Scale Up	Sinopec		China	??			Reported to be Shut In Due to QC Problems with Surfactant				
David		Surtek	Alberta	1985	23		Tertiary			\$0.80	
Driscoll Creek	TRUE	Surtek	Wyoming	1998			Acrylamid converted to acrylate - water cut lowered				
Enigma	Citation	Surtek	Wyoming	2001	24	43	Secondary	In progress		\$2.49	Na2CO3
Etzikom	Renaissance/Husky	Surtek	Alberta	Current			In progress - Information not released				
Gudong	CNPC	Shenli	China	1992	17.4	41.3	Tertiary	55.0%	26.51%	\$3.92	
Isenhaur	Enron	Tiorco	Wyoming	1980	43.1	2.8	Secondary	57.7%	11.58%	\$0.83	Alkali and Polymer Only
Kamay	CNPC	UT/NPER	China	1995	30.3	52.6	Tertiary	60.0%	24.00%	\$4.35	
Lagomar	PDVSA	Surtek	Venezuela	2000	24.8	14.7	Tertiary	45.0%	20.11%	\$4.80	Single Well Test
Mellot Ranch	West	Surtek	Wyoming	2000	22	23	Tertiary	In progress		\$2.51	NaOH
Minas I	Chevron		Indonesia	1999			Micellar Polymer Failed when salinity of slug decreased				
Minas II	Texaco	Texaco	Indonesia	Current			Lignin II Surfactant - In progress - Information not released				
Sho Vel Tum	LeNorman	DOE	Oklahoma	1998	26.4	41.3	Tertiary	60.0%	16.22%	\$6.40	Low Acid Number - Viscous
Beverly Hills	Stocker	Tiorco	California				Surfactant Injectivity Test				
Tanner	Citation	Surtek	Wyoming	2000	21	11	Secondary	In progress		\$2.82	NaOH
West Kiehl	Barnett	Surtek	Wyoming	1987	24	17	Secondary	26.5%	20.68%	\$2.13	
West Moorcroft	KSL	Tiorco	Wyoming	1991	22.3	20	Secondary	20.0%	15.00%	\$1.46	Alkali and Polymer Only
White Castle	Shell	Shell	Louisiana	1987	20	2.8	Tertiary	26.9%	10.10%	\$8.18	No Polymer

Table 3.
 Field cases of ASP EOR.

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